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(54) Title: POLYMER FOAMS CONTAINING BLOCKING AGENTS (57) Abstract An improved closed cell polymer foam and foaming agent involving the use of a hydrogen- containing halocarbon blowing agent (e.g., HCFC-22) in combination with an effective amount of a hydrogen bond forming blocking agent (e.g., organic ether, ester or ketone). The presence of the blocking agent is shown to significantly reduce the escape of blowing agent from and entry of air into the foam resulting in low thermal conductivity over a longer period of time and improved thermal insulation value.		

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POLYMER FOAMS CONTAINING BLOCKING AGENTS

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

 This invention relates to improved polymer
foams and foaming agents by the use of blocking
agents. More specifically, the invention relates to
10 combinations of a hydrogen bond forming blocking agent
and a hydrogen-containing halocarbon and a method of
using the same in closed cell polymer foams to reduce
permeation of air and/or hydrohalocarbon, thereby
maintaining low thermal conductivity and improved
15 thermal insulation value of the foam.

2. Description of Related Art, including
Information Disclosed under §§1.97-1.99

20 It is generally known and an accepted
commercial practice to add a blowing agent to various
polymeric materials during fabrication such as to
produce a cellular (expanded foam) material.
Typically, the blowing agent can be either a reactive
25 solid or liquid that evolves a gas, a liquid that
vaporizes, or a compressed gas that expands during
final fabrication producing the desired polymeric
foam. Such foams are categorically either closed cell
(i.e., non-porous, continuous polymer phase with
30 discontinuous gas phase dispersed therein) or open
cell (porous) foams which are advantageously employed
in various end use applications and exhibit various
advantages associated with the particular type of foam
produced. In describing the closed cell foam as
35 involving a discontinuous gas phase, it should be

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appreciated that this description is an over simplification. In reality the gas phase is dissolved in the polymer phase and there will be a finite substantial presence of gas (blowing agent) in the polymer. Furthermore and as generally known in the art, the cell gas composition of the foam at the moment of manufacture does not necessarily correspond to the equilibrium gas composition after aging or sustained use. Thus, the gas in a closed cell foam frequently exhibits compositional changes as the foam ages leading to such known phenomenon as increase in thermal conductivity or loss of insulation value.

Closed cell foams are usually employed for their reduced thermal conductivity or improved thermal insulation properties. Historically, insulating polyurethane and polyisocyanurate foams have been made using trichlorofluoromethane, CCl_3F (CFC-11), as the blowing agent. Similarly, insulating phenolic foam is known to be made from phenol-formaldehyde resins (typically via an intermediate resole mixture involving a phenol-formaldehyde oligomer condensate) using blends of 1,1,2-trichlorotrifluoroethane, $\text{CCl}_2\text{FCClF}_2$ (CFC-113), and CFC-11 as the blowing agent. Also, insulating thermoplastic foam such as polystyrene foam is commonly manufactured using dichlorodifluoromethane, CCl_2F_2 (CFC-12), as the blowing agent.

The use of a chlorofluorocarbon as the preferred commercial expansion or blowing agent in insulating foam applications is in part based on the resulting k-factor (i.e., the rate of transfer of heat energy by conduction through one square foot of one inch thick homogenous material in one hour where there is a difference of one degree Fahrenheit perpendicularly across the two surfaces of the

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material) associated with the foam produced. Thus, it is generally known and accepted that a chlorofluorocarbon gaseous phase within the closed cell is a superior thermal barrier relative to other inexpensive gases such as air or carbon dioxide. Conversely, the natural intrusion of air into the foam over time and to a lesser extent the escape of the chlorofluorocarbon from the cell is deleterious to the desired low thermal conductivity and high insulative value of the foams. Also, the escape of certain chlorofluorocarbons to the atmosphere is now recognized as potentially contributing to the depletion of the stratospheric ozone layer and contributing to the global warming phenomenon. In view of the environmental concerns with respect to the presently used chlorofluorocarbon blowing agents, it is now generally accepted that it would be more desirable to use hydrochlorofluorocarbons or hydrofluorocarbons rather than the chlorofluorocarbons. Consequently, the need for a method or way of inhibiting the permeation of air and blowing agent through the polymer phase of the polymeric foam exists and hopefully any such solution to the problem would be effective in inhibiting the permeation of the proposed alternative halocarbons.

Historically, various methods and compositions have been proposed, with varying degree of success, to alleviate and/or control problems associated with permeation of gases into and out of polymeric foams. For example, in U.S. Patent 4,663,361 the problem of shrinkage (lack of dimensional stability) associated with using any blowing agent other than 1,2-dichlorotetrafluoroethane in the manufacture of foamed polyethylene is addressed. In this reference, a stability control

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agent is used in either a homopolymer or copolymer of ethylene wherein the blowing agent is isobutane or isobutane mixed with another hydrocarbon or a chlorocarbon, fluorocarbon or chlorofluorocarbon. The stability control agent is either partial esters of long chain fatty acids with polyols, higher alkyl amines, fatty acid amides, olefinically unsaturated carboxylic acid copolymers, or polystyrene. This reference also describes other prior art and is included by reference for such purpose.

In U.S. Patent 4,243,717 a Fischer-Tropsch wax is added to expanded polystyrene beads to produce a stable cell structure in the foam, without specific reference to the permeation of blowing agent or air. In Canadian Patent 990,900 the use of a barrier material or blocking agent is disclosed to alleviate the problem of gas migration through the cell wall specifically at the time of foaming. The particular problem addressed in this Canadian patent is the rupture and total collapse of the cell walls that frequently occur in the manufacture of closed cell polyethylene foam. This problem is attributed to the fact that the cell walls for such foams are permeable to the rapidly expanding gas under the influence of the heat liberated by the exothermic polymer crystallization. The specific solution disclosed in this reference is to use a blend of polyethylene and polypropylene along with a barrier resin such as an elastomer containing polystyrene or acrylic resin which are intended to contribute high melt strength to the cell wall at the foaming temperature. An inert nucleant is also employed along with at least two gaseous propellants of substantially different vapor pressures.

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In U.S. Patent 4,795,763 the use of at least 2 percent carbon black as a filler uniformly dispersed in a polymeric foam is shown to reduce the aged k-factor of the foam to below the aged k-factor of the corresponding unfilled foam.

SUMMARY OF THE INVENTION

The present invention provides a method of preventing or slowing down both the rate of intrusion or permeation of air into the closed cells of a polymeric foam as well as preventing or slowing down the escape of the blowing agent by permeation or migration out of the polymer foam cells. Thus, according to the present invention the effective rate of permeation of air and/or hydrohalocarbon across the polymeric phase of the foam is substantially reduced by virtue of the presence of a blocking agent. Further according to the present invention a blocking agent capable of hydrogen bond formation with the hydrogen-containing halocarbon is incorporated into the polymeric foam and thus tends to form hydrogen bonds with the blowing agent. This in turn dramatically reduces the permeation rate of the hydrogen-containing blowing agent retaining it in the foam. The presence of the blocking agent also functions to reduce entry of air into the polymer foam. By reducing the entry of air into insulating foam and simultaneously reducing the permeation of blowing agents out of insulating foam, the blocking agents according to the present invention produce foams which better maintain their insulating characteristics relative to foams made without these hydrogen bond forming agents.

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Thus, the present invention provides in a closed cell thermoplastic or thermoset polymer foam characterized by a continuous polymeric phase and a discontinuous gaseous phase, the improvement
5 comprising: (a) a gaseous phase comprising at least one hydrogen-containing halocarbon; and (b) an effective amount of a hydrogen bond forming blocking agent. Preferably the hydrogen bond forming blocking agent is an organic ether, ester or ketone and is
10 preferably present in the range of from about 0.1 to about 20 weight percent based on the total weight of foam.

Since the blocking agent according to the present invention can often be conveniently
15 incorporated, marketed and used in combination with the blowing agent, the present invention further provides an improved thermoplastic or thermoset polymer foaming composition comprising:

- (a) a hydrogen-containing halocarbon; and
- 20 (b) an effective amount of a hydrogen bond forming blocking agent.

The improved method according to the present invention involves, in a method of manufacturing an expanded polymeric foam wherein a blowing agent
25 expands as the polymeric phase solidifies, the specific improvement comprising the steps of:

- (a) selecting a hydrogen-containing halocarbon as the blowing agent; and
- (b) adding an effective amount a hydrogen bond
30 forming blocking agent to reduce the permeation of air into the foam or slow down the escape of blowing agent from of the foam.

It is an object of the present invention to provide a blocking agent that when incorporated into a
35 polymeric foam will reduce or prevent the intrusion of

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air into the foam and/or the permeation or escape of blowing agent from the foam. It is a further object of the present invention to provide such a blocking agent that is particularly useful with the

5 hydrogen-containing chlorofluorocarbons and hydrogen-containing fluorocarbons (i.e., the HCFCs and HFCs) in that the blocking agent will hydrogen bond with the hydrohalomethanes and hydrohaloethanes, thus significantly reducing their rate of permeation and

10 escape from a closed cell polymeric foam. It is an associated object of the present invention to provide insulating foam containing a blocking agent and a method of manufacturing the same that exhibits preservation of the insulating properties over longer

15 periods of times relative to the absence of the blocking agent. Fulfillment of these objects and the presence and fulfillment of additional objects will be apparent upon complete reading of the specification and the claims.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Polymer foams typically involve a continuous or at least a contiguous phase in a cellular

25 structure. This cellular structure can be either flexible or rigid and is categorically either an open cell structure (i.e., the individual cells are ruptured or open producing a soft, porous "sponge" foam which contains no blowing agent gas) or a closed

30 cell structure (i.e., the individual cells contain blowing agent gas surrounded by polymeric sidewalls with minimum cell-to-cell gas flow). Thermally insulating foams are closed cell structures containing a blowing agent gas (i.e., a gas formed in situ during

35 the foam manufacturing process). Preferably the

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blowing agent gas should have a low vapor thermal conductivity (VTC) so as to minimize conduction of heat through the insulating foam. Thus, the vapor thermal conductivities for halocarbons such as CFC-11, CFC-12 and hydrochlorodifluoromethane, CHClF_2 (HCFC-22), at 25°C (i.e., 45.1, 55.7 and 65.9 $\text{Btu}\cdot\text{ft}^{-1}\cdot\text{hr}^{-1}\cdot^\circ\text{F}^{-1} \times 10^4$, respectively) compare favorably to the VTC for air at 25°C (i.e., 150.5 $\text{Btu}\cdot\text{ft}^{-1}\cdot\text{hr}^{-1}\cdot^\circ\text{F}^{-1} \times 10^4$). From these data, it can readily be seen that the presence of a halocarbon blowing agent is required for optimum thermal insulation properties with both thermoplastic and thermoset foams.

A problem with hydrogen-containing alternative blowing agent HCFC-22 is its rapid migration from thermoplastic foams. For example, in the case of one grade of polystyrene, the permeation rate at 25°C for CFC-12 vs. HCFC-22 was 4.2×10^{-9} g/hr vs. 6.5×10^{-8} g/hr (i.e., HCFC-22 diffused 15.5 times faster than CFC-12). Without some way to prevent or slow down the rate of HCFC-22 permeation from polystyrene foam, this blowing agent is unacceptable for producing good insulation foam, using this particular grade of polystyrene.

HCFC-22 is also known to diffuse rapidly from some polyurethane/polyisocyanurate foam formulations. Techniques for slowing/preventing this blowing agent migration are required if the halocarbon is to be useful in preparing these thermoset insulating foams.

In addition to the undesirable degradation of foam insulation value caused by permeation losses of blowing agent, the effect of air entry from the atmosphere into the foam cells is at least equally significant. As air enters the foam cells, the vapor

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thermal conductivity of the cell gas increases and the insulation value drops.

5 The blocking agents of this invention unexpectedly function to reduce air entry into foams and/or to reduce the permeation of hydrogen-containing blowing agents such as HCFC-22 from the foam cells, thereby producing more effective/economical insulation foams.

10 For the purposes of the present invention, the term "blocking agent" is used herein to denote hydrogen bond forming compounds which contain ether, ester or ketone groups or the like. These hydrogen bond forming compounds can bond or associate with hydrogen-containing halocarbon blowing agents such as
15 HCFC-22 and thereby reduce their rates of permeation from the foam.

Unexpectedly, HCFC-22, difluoromethane (CH_2F_2 , HFC-32), 1,1,1-trifluoro-2,2-dichloroethane (CHCl_2CF_3 , HCFC-123), 1,1,2-trifluoro-1,2-dichloroethane (CHClFCClF_2 , HCFC-123a), 1,1,1,2-tetrafluoro-2-chloroethane (CHClFCF_3 , HCFC-124), pentafluoroethane (CHF_2CF_3 , HFC-125), 1,1,2,2-tetrafluoroethane (CHF_2CHF_2 , HFC-134), and 1,1,1,2-tetrafluoroethane (CH_2FCF_3 , HFC-134a) have been
20 observed to associate or hydrogen bond with compounds containing ether, ester or ketone groups. Glycols and other polyhydroxy compounds tend to form intra- or inter-molecular hydrogen bonds with themselves and thus do not associate strongly with HCFC-22. HCFC-22, with hydrogen bonding esters, ketones or ethers,
25 exhibits dramatically reduced vapor pressure as a result of the association. Furthermore, when these hydrogen bonding compounds are present in thermoplastic polymers such as polystyrene, the permeation of
30 HCFC-22 is reduced/slowed as the result of the mutual
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association which occurs between these compounds. The hydrogen bond forming agents additionally function to improve the solubility of blowing agents such as HFC-134a in thermoplastic polymers such as polystyrene.

Also, the mutual solubility of HCFC-22 and HCFC-123 or the like with several hydrogen bond forming compounds further provides evidence of an unexpected association between these materials.

CFC-12 does not share this unexpected solubility characteristic. Because of the solubility of many of the hydrogen bond forming compounds in HCFC-22, these compounds are suitable for dissolving in HCFC-22 and, thus, can be made commercially available in this convenient form.

For purposes of the present invention and as previously mentioned, the blocking agent can broadly be any compound that contains either an ether, ester or ketone group or combinations of the same and is capable of hydrogen bonding or the equivalent strong association or complexing with hydrogen-containing halocarbons. For example, but not by way of limitation, the following table lists examples of ether, ester or ketone groups containing compounds which associate or hydrogen bond with hydrogen-containing halocarbons such as HCFC-22.

HYDROGEN BONDING AGENTS

- (1) Polyethylene oxide polymers
- (2) Ethylene oxide/propylene oxide copolymers
- (3) Polypropylene oxide polymers
- (4) Polyethylene glycol mono- and dioleates
- (5) Polyethylene glycol monostearates
- (6) Alkylphenoxy polyethoxy ethanols

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- (7) Polyethylene oxide sorbitan monostearates and tristearates
- (8) Polyethylene oxide fatty acid amides
- (9) Primary and secondary alcohol ethoxylates
- 5 (10) Glyme, diglyme, triglyme and tetraglyme
- (11) Mono-, di- and tripropylene glycol methyl ethers and ether acetates
- (12) Dimethyl adipate, succinate and glutarate
- (13) Ethylene oxide/propylene oxide adducts with a
10 sucrose
- (14) Ketones and polyketone polymers.

The use of hydrogen-containing blowing agents such as HCFC-22 with ether, ester or ketone
15 hydrogen bond forming compounds in polymer foams does not preclude the simultaneous incorporation of blowing agents such as 1,1-dichloro-1-fluoroethane (CCl_2FCH_3 , HCFC-141b), 1-chloro-1,1-difluoroethane (CClF_2CH_3 , HCFC-142b), 1,1,1-trifluoroethane (CF_3CH_3 , HFC-143a),
20 1,2-difluoroethane ($\text{CH}_2\text{FCH}_2\text{F}$, HFC-152), and 1,1,-difluoroethane (CHF_2CH_3 , HFC-152a) which do not tend to form strong hydrogen bonds. It should be further appreciated that various CFCs may also be present as a component of a blowing agent mixture
25 useful according to the present invention and that the present invention is applicable when CO_2 , hydrocarbons or methyl formate are components of the blowing agent gas. Similarly, various additives such as stabilizers, dyes, fillers, and the like can be
30 present in the blowing agent.

In addition to reducing the entry of air into and/or the migration of hydrogen-containing blowing agents such as HCFC-22 from thermoplastic
35 foams, the hydrogen bond forming agents may provide

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other functions to the foam manufacturing process. For example, compounds such as the polyethylene oxide polymers may provide lubricity and thereby increase the extrusion throughput or production rate.

5 Furthermore, these compounds are contemplated as potentially useful as polymer plasticizers and may contribute advantageously to other properties.

The hydrogen bond forming agents of this invention are suitable for use with thermoplastics
10 such as polystyrene, polyethylene, polypropylene, polyvinyl chloride, and the like to prevent loss of hydrogen-containing blowing agents; however, they can also be used with thermoset polymer foams such as polyurethane, polyisocyanurate, and phenolic resin
15 foams. Since these hydrogen bond forming agents associate with blowing agents such as HCFC-22, they will function to reduce/prevent permeation of the blowing agent in any compatible polymer foam system. Furthermore, these hydrogen bond forming agents will
20 function in the presence of other additives normally used in polymer foams, such as stabilizers, dyes, fillers, and the like.

The blowing agent concentration used to prepare most conventional thermoplastic and thermoset
25 polymer foams is generally in the range of about 5 weight percent to about 30 weight percent (based on total weight of the foam). To reduce migration of hydrogen-containing blowing agents such as HCFC-22, the effective use concentration of hydrogen bond
30 forming agent is at least about 0.1 weight percent and preferably from about 1.0 to 20 weight percent (based on total formulation weight), most preferably about 0.5 weight percent to about 10 weight percent. Typically, the improved polymer foaming composition
35 will contain from 1 to 100 parts by weight hydrogen

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bond forming blocking agent for every 100 parts of hydrogen-containing halocarbon blowing agent.

The actual method by which the blocking agent according to the present invention is to be incorporated into the closed cell foam can vary according to the specific application and composition being employed. In the broadest sense, the blocking agent can be treated as any other foam additive as generally known in the art. As previously stated, the blocking agent in certain applications imparts beneficial effects to the polymer phase in addition to reducing permeability and in such cases the blocking agent can be added to the polymer. Since the blocking agent is categorically a hydrogen bond forming compound, it may be advantageously added to the blowing agent or preblended into the polymer (e.g., polystyrene) prior to extrusion or other method of fabrication. In the case of thermoset foams (e.g., polyurethane/polyisocyanurate foams) the hydrogen bond forming agents can be added to the foam in the isocyanate (A-side) or the polyol (B-side) or added with the blowing agent at the mixing head where the A-side and B-side are combined (i.e., third-streamed). For purposes of the present invention the term "A-side" is used to specify the isocyanate containing component of a conventional two component precursor foam system. The term "B-side" is used to specify the polyol containing component. It should be appreciated that this nomenclature may be reversed particularly in certain European literature. It should be further appreciated that these precursor components to foams typically contain other ingredients, additives, agents, diluent and the like all as generally known in the art. Thus for example, but not by way of limitation, the B-side will typically contain, in

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addition to the polyol, a surfactant, a catalyst and one or more blowing agents. If the hydrogen bond forming agent used contains free hydroxyl groups, this must be taken into account when calculating the hydroxyl equivalent for the B-side system. In the case where the blocking agent is preferentially more soluble in one of the foam components, it is preferably added to that component. For example, addition of the blocking agent to the polyol component of two-component thermoset resin is preferred. Of course, the addition to more than one component or either component is also contemplated. In the case of phenolic foams, the hydrogen bond forming agents can be added to the foam by preblending into the resole or added separately at the mixing head prior to the foam laydown. The most preferred method of adding the blocking agent is to mix it with the blowing agent and as such the admixture of HCFC or HFC and blocking agent is contemplated as being a commercially attractive product, per se. Again, since the blocking agent is categorically a hydrogen bond forming compound, in the case of the thermoset foams (e.g., polyurethane/polyisocyanurate foams) not only can a polyol be added as the blocking agent but the polyol (B-side) can be viewed as the blocking agent. Thus, as previously stated if the hydrogen bond forming agent used contains free hydroxyl groups they must be taken into account when calculating they hydroxyl equivalent for the B-side system. Conversely, the ether and ester groups of the polyol found in the B-side should also be viewed as contributing as the hydrogen bond forming blocking agent. As such, in cases where there are ether and/or ester groups present in the polyol, the polyol should be considered as a blocking agent.

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The following examples are presented to further illustrate specific critical properties of various specific embodiments of the present invention, including vapor pressure, boiling point and permeation data, as well as similar properties, for comparison purposes, of systems and compositions outside the scope of the invention.

EXAMPLE 1

The solubilities of several representative hydrogen bond forming agents in HCFC-22 were determined for 10 wt. % solutions at ambient temperature (approximately 70°F). The solutions were prepared by combining the hydrogen bond forming agents with HCFC-22 in 4 oz. plastic-coated pressure bottles. Solubility was determined by visual examination. Table I lists ten hydrogen bond forming compounds which are soluble to >10 wt. % in HCFC-22. These hydrogen bond forming agents are soluble in HCFC-22, HCFC-123 and HCFC-123a because of their bonding or association; whereas, they are generally insoluble in CFC-12. The hydrogen bond forming agents are also soluble in HCFC-141b.

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Table I
Hydrogen Bonding Agent Solubility in HCFC-22

5 The following hydrogen bonding agents are soluble at ambient temperature in HCFC-22 to >10 wt. %:

Hydrogen Bonding Agents*

10 "PLURONIC" F-108
 "CARBOWAX" 3350
 "WITCONOL" H35A
 "TRITON" X-67
 Polypropylene Glycol 2025
15 "ETHOFAT" 0/20
 "ETHOMID" HT/60
 "TERGITOL" 15-S-20
 "ETHOX" DO-9
 "TERGITOL" NP-40

20 * Solubilities determined at ambient temperature (approximately. 70°F). Similar solubilities have been observed for HCFC-123, HCFC-123a, and HCFC-141b even though HCFC-141b is not a strong hydrogen bond forming
25 HCFC.

EXAMPLE 2

 Vapor pressure data were obtained for mixtures of CFC-12 and HCFC-22, respectively, with
30 hydrogen bonding agents. In these tests, 30 grams of blowing agent was combined with 70 grams of hydrogen bond forming agent in a 4 oz. plastic-coated pressure bottles. After thermostating the bottles at 70°F, the vapor pressures were determined using a pressure
35 gauge accurate to 0.1 psi. Although HCFC-22 by itself

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has considerably higher vapor pressure at 70°F than CFC-12 (121.4 psig vs. 70.2 psig), the formation of hydrogen bonds between the hydrogen bond forming agents and HCFC-22 resulted in dramatic vapor pressure depressions to values much lower than for CFC-12. The vapor pressure data are summarized in Table II.

Boiling point data were obtained for a 30/70 blend of HCFC-123/DBE. The data in Table IIA show an elevation in boiling point (relative to the value calculated from Raoult's Law) of 17°C as the result of the association or hydrogen bonding which occurs between these materials. Similar boiling point elevations were observed for 30/70 blends of HCFC-123/DPM and HCFC-123/DPMA.

Table IIB shows vapor pressure data for HFC-32, HCFC-124, HFC-125, HFC-134 and HFC-134a with DBE, acetone, and 2-pentanone. Each hydrogen bond forming agent depresses the vapor pressure of the blowing agents.

Table II
Effect of Hydrogen Bonding Agents
on Vapor Pressure of HCFC-22

Bonding Agent	Blowing Agent	Vapor Pressure at 70°F, psig	
	Wt. %	CFC-12	HCFC-22
None	100.0	70.2	121.4
"CARBOWAX" 3350	30.0	70.2	57.2
"PLURONIC" F-108	30.0	70.2	55.5
"WITCONOL" H35A	15.0	44.0	20.0
	30.0	70.2	38.0(*)
"TRITON" X-67	15.0	70.2	29.5
	30.0	70.2	41.0
"TWEEN" 61	30.0	70.2	70.5

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Polypropylene Glycol			
	2025	30.0	49.2(*) 39.3(*)
	"ETHOFAT" 0/20	30.0	57.5(*) 35.0(*)
	"ETHOMID" HT/60	15.0	70.2 18.5
5		30.0	70.2 29.0
	"CARBOWAX" 8000	30.0	70.2 61.0
Polyethylene Glycol			
	Cpd 20M	30.0	70.2 55.2
	"POLYOX" WSRN-10	30.0	70.2 56.5
10	"TERGITOL" 15-S-20	15.0	70.2 15.0
		30.0	70.2 26.5(*)
	"TERGITOL" 24-L-92	30.0	59.2(*) 31.0(*)
	"TERGITOL" NP-40	30.0	70.2 44.0
Polypropylene Glycol			
15	425	30.0	54.0(*) 37.0(*)
			(112.5 at (93.0 at
			130°F) 130°F)
	"PLURACOL" 975	15.0	46.0(*) 17.0(*)
			(110.0 at (49.0 at
20			130°F) 130°F)
		30.0	70.2 50.5(*)
			(2 phases)
	"ETHOX" DO-9	30.0	53.7(*) 39.5(*)
	Diglyme	30.0	26.0(*) 7.0(*)
25	Glyme	30.0	16.0 2.5(*)
	DBE	30.0	45.0(*) 21.5(*)
	"ARCOSOLV" PM	30.0	35.0(*) 19.5(*)
	Acetone	30.0	19.5(*) 5.9(*)
	2-Pentanone	30.0	40.5(*) 14.5(*)
30	Polymethylvinyl Ketone	30.0	61.0(*) 45.5(*)

(* solution)

Table IIA
Boiling Point Elevation Data

5		<u>Boiling Point, °C</u>	
	<u>Compound</u>	<u>Actual</u>	<u>Raoult's Law</u>
	HCFC-123*	27.6	--
	DBE	196	--
	30/70 HCFC-123*/DBE	81	64
10	DPM	188	--
	30/70 HCFC-123*/DPM	88	67
	DPMA	200	--
	30/70 HCFC-123*/DPMA	93	60

15 * Commercial grade; typically including
 up to about 10 percent HCFC-123a.

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-20-

Table IIB

Effect of Hydrogen Bonding Agents
on Vapor Pressures of

HCFC-124, HFC-125, HFC-134, HFC-134a and HFC-32

10	<u>Bonding Agent</u>	Blowing		
		<u>Blowing Agent</u>	<u>Agent Wt. %</u>	<u>Vapor Pressures at 70°F, psig</u>
	None	CFC-114	100.0	12.9
	DBE	CFC-114	30.0	12.7 (*)
	None	HCFC-124	100.0	34.1
	DBE	HCFC-124	30.0	1.2 (*)
15	Acetone	HCFC-124	30.0	0 (*)
	2-Pentanone	HCFC-124	30.0	1.8 (*)
	None	HFC-125	100.0	163.8
	DBE	HFC-125	30.0	35.0 (*)
	Acetone	HFC-125	30.0	10.0 (*)
20	None	HFC-134a	100.0	81.3
	DBE	HFC-134a	30.0	15.3 (*)
	Acetone	HFC-134a	30.0	3.5 (*)
	2-Pentanone	HFC-134a	30.0	12.0 (*)
	None	HFC-134	100.0	60.2
25	DBE	HFC-134	30.0	7.0 (*)
	Acetone	HFC-134	30.0	0 (*)
	None	HFC-32	100.0	206.3
	Acetone	HFC-32	30.0	41.0 (*)
30	(* solution)			

EXAMPLE 3

For comparison purposes, HCFC-22 was
combined with non-hydrogen bonding agents, such as
stearyl stearamide ("KEMAMIDE" S-160) and glycerol

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monostearate ("WITCONOL" MST), and the vapor pressure of HCFC-22 showed slight, if any, depression. Thus, compounds which form strong hydrogen bonds with themselves, e.g., glycerol monostearate, do not
 5 associate with HCFC-22 and do not reduce the measured vapor pressure. The vapor pressure data are shown in Table III.

Table III

Vapor Pressure for HCFC-22
with Non-Hydrogen Bonding Agents

	Additive	Blowing Agent	Vapor Pressure at 70°F. psig	
		Wt. %	CFC-12	HCFC-22
	None	100.0	70.2	121.4
	"KEMAMIDE" S-180	30.0	70.2	121.4
20	"WITCONOL" MST	30.0	70.2	118.0
	"ALKAMIDE" HTDE	30.0	70.2	105.0
	"ARMID" O	30.0	70.2	118.0
	"SPAN" 60	30.0	70.2	108.5
	Glycerin	30.0	70.2	121.4
25	"SELAR" OH 3007	30.0	70.2	121.4
	"SELAR" PA 7426	30.0	70.2	121.4
	"SURLYN" 8396-2	30.0	70.2	121.4
	Polyacrylonitrile A-7	30.0	70.2	120.8
	"SOLEF" 1008-1001	30.0	70.2	121.4
30	"ELVANOL" 90-50	30.0	70.2	121.4

EXAMPLE 4

The permeation of nitrogen and HCFC-22 through polystyrene film was measured for polymer
 35 films with and without blocking agents.

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The permeation data was obtained on 15-20 mil thick polystyrene films which were prepared as follows:

- 5 (a) Hydrogen bond forming agents and polystyrene were passed through a twin screw extruder three times at 400°F to ensure good blending of components. The extruder used was a 28 mm Werner and Pfleider, Stuttgart, Model 20S-K-28 twin screw.
- 10 (b) After pelletizing the extruded polymer, 15-20 mil thick films (in 6" x 6" sheets) were pressed at about 35,000 psig pressure using a Barber-Coleman press.
- 15 (c) The 6" x 6" sheets of 15-20 mil film were cut into 47 mm diameter circles or discs with a polymer die punch.

Permeation tests were run on polystyrene films containing various blocking agents to determine the permeation of air and blowing agents in polystyrene foam. Such film closely simulates polystyrene foam cell walls and the permeation data are predictive of foam blowing agent retention and susceptibility to air intrusion. Studies were made with HCFC-22 and nitrogen (simulating air).

Polystyrene Film Preparation

25 (A) Mixing Polystyrene/Additives by Extrusion

Samples of polystyrene (2500 grams) plus blocking agents were hand mixed and passed through a screw extruder three times at about 400°F. Three passes were used to ensure uniform blending of components. Since the polymer mixes were extruded into a water tank for cooling prior to pelletizing (between the passes through the extruder and after the third extrusion), the pelletized samples were dried about 16 hours in a vacuum oven at 175-200°F. The

35

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extruder used was a 28 mm Werner and Pfleider, Stuttgart, Model 20S-K-28 twin screw.

(B) Film Pressing of Polystyrene/Additive Mixtures

5 Using a Barber-Coleman press, 30 gram samples of polystyrene/additive mixes (as pellets) were pressed into 6" x 6" sheets of film with 15-20 mil thickness. The pressing was done at 400°F and at a pressure of about 35,000 psig (maintained for 5
10 minutes).

(C) Film Discs for Permeation Tests

Discs (15-20 mil thickness) were cut from 6" x 6" sheets of film. Five discs of 47 mm diameter were made from each sheet. The discs were cut or
15 stamped at ambient temperature using a die punch made of A-2 type steel (hardened).

Permeation Test Procedure

The permeation tests on the polystyrene film containing blocking agents were conducted by a
20 modification of ASTM D1434-82, "Standard Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting". This modified procedure is described in the Master of Chemical Engineering Thesis, P. S. Mukherjee, Widener University, Chester, PA, February 1988, entitled "A Study of the Diffusion
25 and Permeation Characteristics of Fluorocarbons Through Polymer Films".

Test Conditions

(1) All tests were run at a 20 psia pressure
30 differential between the high pressure side and the low pressure side of the permeation cell.

(2) Permeation tests were run at 60 to 120°C, with tests for each blocking agent/polystyrene/gas combination being run at two or more temperatures.

35

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Data for other temperatures were calculate from the equation :

$$\ln P = \frac{A}{T} + B$$

where P is permeation coefficient, T is °K (°C + 273.2) and A and B are constants determined from the permeation coefficients calculated from the following equation :

$$P = \frac{(\text{Rate of Permeation})(\text{Film Thickness})}{(\text{Film Area})(\text{Pressure drop across film})}$$

(3) The permeation rates are based on a 1 cm² by 1 cm thick film with a 1.0 psia pressure drop across the film.

The permeation rate and permeation coefficient data for nitrogen in polystyrene containing blocking agents are summarized in Table IV. Data for HCFC-22 in polystyrene containing blocking agents are shown in Table V. The units for permeation rate are g/hr and for permeation coefficient are cm³(STP)·cm/sec·cm²·cmHg. The data summarized in Tables IV and V are calculated at 25°C from data measured at other temperatures.

Table IV

Permeation Data

Polymer: Polystyrene* Temperature: 25°C

<u>Gas</u>	<u>Blocking Agent</u>	<u>Wt. % in Polymer</u>	<u>Permeation Coeff.</u>	<u>Permeation</u>	<u>% Change In</u>
			<u>cm³ gas at STP cm sec cm² (cm Hg)</u>	<u>Rate g/hr</u>	<u>Permeation Rate</u>
Nitrogen	None	-	8.00 x 10 ⁻¹¹	1.86 x 10 ⁻⁹	-
Nitrogen	"WITCOHOL"	5.0	5.50 x 10 ⁻¹¹	1.28 x 10 ⁻⁹	-31.2

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E35A					
5	Nitrogen	"TRITON" X-67	5.0	4.49×10^{-11}	1.04×10^{-9}
	Nitrogen	Polypropylene	5.0	4.72×10^{-11}	1.10×10^{-9}
	Glycol 2025				
	Nitrogen	"TWEEN" 61	5.0	4.672×10^{-11}	1.07×10^{-9}

-42.5

* "DYLENE" 8 polystyrene (Melt Index 6-7), Arco Chemical Company.

10

Table VPermeation Data

Polymer: Polystyrene* Temperature: 25°C

15

Permeation					
<u>Gas</u>	<u>Blocking Agent</u>	<u>Wt. % in Polymer</u>	<u>Coefficient</u>	<u>Permeation Rate</u>	<u>% Change In Permeation Rate</u>
			<u>cm³ gas at STP cm sec cm² (cm Hg)</u>	<u>g/hr</u>	<u>Rate</u>
20 HCFC-22	None	-	5.41×10^{-12}	3.89×10^{-10}	-
HCFC-22	"WITONOL"	5.0	2.21×10^{-12}	1.58×10^{-10}	-59.4

E35A

* "DYLENE" 8 polystyrene (Melt Index 6-7), Arco Chemical Company.

25

Example 5

In a manner analogous to Example 2, vapor pressure data were obtained for mixtures of HCFC-22 in polyols and for a mixture of HFC-134a in a polyol. The vapor pressure data are summarized in Table VI.

30

Table VI

Effect of Polyols as
Hydrogen Bonding Agents
on Vapor Pressure
of HCFC-22 and HFC-134a

35

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		Blowing Agent	Vapor Pressure at 70°F, psig	
Hydrogen		Wt. %	FOUND	RAOULT'S
LAW				
5	<u>Hydrogen Bonding</u>		<u>HCFC-22*</u>	
	STEPANPOL PS-2502	2.9	0	15.2
		5.4	13.5	27.7
		7.8	17.0	37.0
		17.9	43.5	64.5
10		20.6	64.0	68.0
	PLURACOL P-410	2.0	0	11.0
		4.0	0	20.6
		6.0	3.0	29.0
		8.0	6.5	36.3
15		10.0	9.0	42.9
		12.0	10.6	48.9
	PLURACOL TP-440	2.1	4.3	11.6
		4.0	7.8	20.6
		6.4	12.0	30.5
20		9.9	18.5	42.6
		12.0	24.2	48.9
	PLURACOL 1016	1.8	0.8	7.3
		4.0	4.8	15.3
		6.0	8.0	22.0
25		8.2	15.0	28.7
		10.1	17.0	33.2
		12.1	20.5	39.2
Blocking Agent		Wt. %	FOUND	RAOULT'S
LAW				
30	<u>Bonding Agent</u>		<u>HFC-134A*</u>	
	PLURACOL PT-440	2.5	0	6.8
		5.0	4.0	12.7
		7.6	12.0	18.1
		10.0	19.0	22.4
35	* wt% blowing agent in hydrogen bonding agent			

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Example 6

To further verify the differences in behavior between the conventional chlorofluorocarbon blowing agents and the hydrogen-containing halocarbons, the solubility of HCFC-134a was compared to that of CFC-12. The CFC-12 was found to be miscible at 25°C in 150 SUS (32cs at 100°F) oils including paraffinic oils, naphthenic oils, alkylated benzene oils and PAG* oils. In contrast, the HFC-134a was found to be insoluble (<1 wt. percent) in the paraffinic oils, naphthenic oils and alkylated benzene oils. However, HFC-134a was found to be miscible in PAG oils at 25°C.

* UCON oils (n-butyl alcohol + propylene oxide or EO/PO)

Example 7

Closed cell polyurethane thermoset foams were produced using CFC-11, HCFC-22 and HFC-134a as the primary blowing agent and CO₂ produced in situ by addition of water. The K-factor for the respective foams were measured and compared to vapor thermal conductivity data corresponding to the blowing agents. The respective recipe for both the A-side and the B-side components and the resulting data are presented in Table VII along with the vapor thermal conductivity data.

Table VII

Foams co-blown with water:

A-Side	270 gms	PAPI 580
B-Side	100 gms	STEPAPNOL PS-2502
	2.3 gms	DC 193
	5 gms	HEXCEM 977

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.35 gms POLYCAT 8
 2.5 gms water
 (see below) halocarbon

Foam Index** 250

5	Blowing	B-Side	Volume of gas				
	K-factor*						
	Agent	vap. pres.		MOLES		Density	age
	in days @ R.T.						
	<u>type</u>	<u>gms</u>	<u>psig</u>	<u>B.A.</u>	<u>CO₂</u>	<u>total lbs/ft³</u>	<u>5</u>
10	<u>6</u>						
	CFC-11	12	0	0.09	0.14	0.23	0.171
	CFC-11	22	0	0.16	0.14	0.30	0.162
	CFC-11	32.6	0	0.24	0.14	0.38	0.151
	HCFC-22	12	33	0.14	0.14	0.28	0.162
15	HFC-134a	12	28	0.12	0.14	0.26	2.97
							0.172

Foams blown without water:

	A-Side	158	gms	PAPI 580
20	B-Side	100	gms	STEPANPOL PS-2502
		1.7	gms	DC 193
		1.35	gms	HEXCEM 977
		.17	gms	POLYCAT 8
		0.0	gms	water
25	(see below) halocarbon			

Foam Index** 250

	Blowing	B-Side		Volume of gas			
	K-factor*						
	Agent	vap. pres.		MOLES		Density	age
30	in days @ R.T.						
	<u>type</u>	<u>gms</u>	<u>psig</u>	<u>B.A.</u>	<u>CO₂</u>	<u>total lbs/ft³</u>	
	<u>10</u>						
	CFC-11	41	0	0.30	0.00	0.30	2.5
	0.143						

35

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HCFC-22 26 0 0.30 0.00 0.30 2.8
0.162

VAPOR THERMAL CONDUCTIVITY DATA

5	BLOWING AGENT	VTC, Btu/hr·ft·°F	
		25°C	60°C
	CFC-11	0.00451	0.00530
	CFC-22	0.00660	0.00748
	HFC-134a	0.00838	0.01020
	CO ₂	0.00953	0.01107

10

* (Btu·in/hr·ft²·°F)

** (equivalents of isocyanate/equivalents of hydroxyl)x100

15 The primary property of halocarbon blowing agents in insulating foam is to provide good thermal insulation by virtue of their low vapor thermal conductivity in the foam cells. By comparing the accompanying vapor thermal conductivity data (VTC) for CFC-11, and HFC-134a or CFC-22, it is apparent that conductivity of HFC-134a and CFC-22 is almost twice that of CFC-11. Thus it is to be expected that an insulating foam made with HFC-134a or CFC-22 would be a much poorer insulator than a foam made with CFC-11. On the contrary and as seen in the k-factor data, the insulation performance for the HFC-134a/CO₂ and CFC-22/CO₂ foam is unexpectedly and essentially the same as that for the CFC-11/CO₂ foam, wherein the HCFC-134a/CO₂ and CFC-22/CO₂ foam produced in the presence of the blocking agent exhibited extremely fine closed cell structure.

The chemicals used in the previous Examples and tests are identified structurally and by source as follows:

30	<u>Designation</u>	<u>Structure</u>	<u>Source</u>
	"CARBOWAX" 3350	Polyethylene	Union Carbide Corp.
			glycol
	"CARBOWAX" 8000	Polyethylene	Union Carbide Corp.
			glycol
	"Pluronic" F-108	Ethylene	BASF Wyandotte Corp.
35		oxide/propylene	

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		oxide copolymer	
	"WITCONOL" H35A	Polyethylene glycol (400)	Witco Corp.
		stearate	
5	"WITCONOL" MST	Glycerol monostearate	Witco Corp.
	"TRITON" X-67	Alkylpoly-ethoxy ethanol	Rohm and Haas Co.
	"TWEEN" 61	POE (4) sorbitan stearate	ICI Americas, Inc.
10	Polypropylene Glycol 2025	Polypropylene glycol	Union Carbide Corp.
	"ETHOFAT" 0/20	Polyethylene oxide oleate	Akzo Chemie America
15	"ETHOMID" HT/60	Polyethylene oxide fatty acid amide	Akzo Chemie America
	Polyethylene Glycol Cpd 20M	Polyethylene glycol	Union Carbide Corp.
20	"POLYOX" WSRN-10	Polyethylene oxide	Union Carbide Corp.
	"TERGITOL" 15-S-20	Linear alcohol/ethylene oxide	Union Carbide Corp.
25	"TERGITOL" 24-L-92	Linear alcohol/ethylene oxide	Union Carbide Corp.
	"TERGITOL" NP-40	Nonylphenol/ethylene oxide	Union Carbide Corp.
30	Polypropylene Glycol 425	Polypropylene glycol	Union Carbide Corp.
	"PLURACOL" 975	Sucrose polyol	BASF Wyandotte Corp.
35	"PLURACOL" P-410	Polypropylene glycol	BASF Wyandotte Corp.

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	"PLURACOL" P-440	Trifunctional BASF Wyandotte Corp. polyol based upon Polypropylene glycol
5	"PLURACOL" 1016	Trifunctional BASF Wyandotte Corp. amino polyol
	"STEPANPOL" PS-2502	Difunctional Stepan Company polyol based upon Phthalic anhydride
10	"PAPI" 580	Methylene DOW Chemicals diisocyanate
	"DC" 193	Silicone DOW Chemicals surfactant
15	"HEXCEM" 977	Potassium Mooney Chemicals octanoate
	"POLYCAT" 8	N,N-dimethyl- Air Products and cyclohexylamine Chemicals, Inc. --
	"ETHOX" DO-9	Polyethylene Ethox Chemicals Inc. glycol dioleate
20	Glyme	Ethylene Aldrich Chemical Co. glycol di- methylether
	Diglyme	2-Methoxy- Aldrich Chemical Co. ethyl ether
25	DBE	Mixture of Du Pont Co. dimethyl adipate, dimethyl gluta- rate and di- methyl succinate*
30	"ARCOSOLV" PM	Propylene Arco Chemical Co. glycol mono- ethyl ether
35	"ARCOSOLV" DPM	Dipropylene Arco Chemical Co. glycol mono-

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		methyl ether	
	"ARCOSOLV" DPMA	Dipropylene glycol mono-methyl ether acetate	Arco Chemical Co.
5	"KEMAMIDE" S-180	Stearyl stearamide	Witco Corp.
	Acetone	---	Fisher Scientific
	2-Pentanone	Methyl propyl ketone	Pfaltz and Bauer, Inc.
10	"ALKAMIDE" HTDE	stearic diethanolamide	Alkaril Chemicals, Ltd
	"ARMID" O	Oleamide	Akzo Chemie America
	"SPAN" 60	Sorbitan stearate	ICI Americas, Inc.
15	Glycerin	---	Aldrich Chemical Co.
	"SELAR" OH 3007	Ethylene/vinyl alcohol copolymer	Du Pont Co.
20	"SELAR" PA 7426	Amorphous nylon	Du Pont Co.
	"SURLYN" 8396-2	Ethylene/methacrylic acid copolymer	Du Pont Co.
25	Polymeric Acrylonitrile A-7	Acrylonitrile/methyl acrylate copolymer	Du Pont Co.
	"SOLEF" 1008-1001	Polyvinylidene fluoride	Soltex Polymer Corp.
30	"ELVANOL" 90-50	Polyvinyl alcohol	Du Pont Co.
	"DYLENE" 8	Polystyrene	Arco Chemical Co.
	Polymethylvinyl Ketone (8919)	---	Monomer-Polymer Laboratories, Inc.

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	CFC-12	Dichlorodifluoro-	Du Pont Co.
		methane	
	CFC-114	1,2-dichlorotetra-	Du Pont Co.
		fluoroethane	
5	HCFC-22	Chlorodifluoro-	Du Pont Co.
		methane	
	HCFC-123	1,1,1-trifluoro-2,2	Du Pont Co.
		-dichloroethane	
	HCFC-123a	1,1,2-trifluoro-1,2	Du Pont Co.
10		-dichloroethane	
	HCFC-124	1,1,1,2-tetrafluoro-	Du Pont Co.
		chloroethane	
	HFC-125	Pentafluoroethane	Du Pont Co.
	HFC-32	Difluoromethane	Du Pont Co.
15	HFC-134	1,1,2,2-tetrafluoro-	Du Pont Co.
		ethane	
	HFC-134a	1,1,1,2-tetrafluoro-	Du Pont Co.
		ethane	
	HCFC-141b	1-fluoro-1,1-di-	Du Pont Co.
20		chloroethane	
	* 17/66/16.5 mixture of esters		

Having thus described and exemplified the invention with a certain degree of specificity, it should be appreciated that the following claims are not to be so limited but are to be afforded a scope commensurate with the wording of each element of the claims and equivalents thereof.

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We claim:

1. In a closed cell thermoplastic or thermoset
5 polymer foam characterized by a continuous
polymeric phase and a discontinuous gaseous phase,
the improvement comprising:
 (a) a gaseous phase comprising at least one
hydrogen-containing halocarbon; and
10 (b) an effective amount of a hydrogen bond
forming blocking agent to reduce the
permeation of air into the foam or slow down
the escape of blowing agent from the foam.
- 15 2. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 1 wherein said
hydrogen bond forming blocking agent is selected
from the group consisting of: an organic ether,
ester, ketone or mixtures thereof.
- 20 3. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 1 or 2 wherein
said hydrogen bond forming blocking agent is
present in the range of at least about 0.1 weight
25 percent of said foam.
4. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 1 or 2 wherein
said hydrogen bond forming blocking agent is
30 present in the range of from about 1.0 to about 20
weight percent of said foam.
5. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 1 wherein said
35

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blocking agent is selected from the group consisting of:

- 5 Polyethylene oxide polymers;
Ethylene oxide/propylene oxide copolymers;
Polypropylene oxide polymers;
Polyethylene glycol mono- and dioleates;
Polyethylene glycol monostearates;
Alkylphenoxy polyethoxy ethanols;
Polyethylene oxide sorbitan monostearates and
10 tristearates;
Polyethylene oxide fatty acid amides;
Primary and secondary alcohol ethoxylates;
Glyme, diglyme, triglyme and tetraglyme;
Mono-, di- and tripropylene glycol methyl
15 ethers and ether acetates;
Dimethyl adipate, succinate and glutarate;
Ethylene oxide/propylene oxide adducts with a
sucrose;
Ketones and polyketone polymers; and
20 mixtures thereof.

6. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 1 wherein said
halocarbon is selected from the group consisting
25 of:

CHClF_2 ; CH_2F_2 ; CHCl_2CF_3 ; CHClFCClF_2 ;
 CHClFCF_3 ; CHF_2CF_3 ; CHF_2CHF_2 ; CH_2FCF_3 and
mixtures thereof.

- 30 7. An improved closed cell thermoplastic or
thermoset polymer foam of Claim 6 further
comprising a second blowing agent gas selected
from the group consisting of:

35 CFCl_3 ; CF_2Cl_2 ; $\text{CCl}_2\text{FCClF}_2$; $\text{CClF}_2\text{CClF}_2$;
 CCl_2FCH_3 ; CClF_2CH_3 ; $\text{CH}_2\text{FCH}_2\text{F}$; CH_3CF_3 ;

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CHF_2CH_3 ; CO_2 ; C_3 to C_6 hydrocarbons; methyl formate; and mixtures thereof.

- 5 8. An improved thermoplastic or thermoset polymer foaming composition comprising:
- (a) a hydrogen-containing halocarbon; and
- (b) an effective amount of a hydrogen bond forming blocking agent to reduce the permeation of air into the foam or slow down the escape of blowing agent from the foam.
- 10
9. An improved polymer foaming composition of Claim 8 wherein said hydrogen bond forming blocking agent is selected from the group consisting of: an organic ether, ester, ketone or mixtures thereof.
- 15
10. An improved polymer foaming composition of Claim 8 or 9 wherein for every 100 grams of said hydrogen-containing halocarbon there is from about 1 to about 100 grams of said hydrogen bond forming blocking agent.
- 20
11. An improved polymer foaming composition of Claim 8 wherein said hydrogen bonding blocking agent is selected from the group consisting of:
- 25 Polyethylene oxide polymers;
- Ethylene oxide/propylene oxide copolymers;
- Polypropylene oxide polymers;
- 30 Polyethylene glycol mono- and dioleates;
- Polyethylene glycol monostearates;
- Alkylphenoxy polyethoxy ethanols;
- Polyethylene oxide sorbitan monostearates and tristearates;
- 35 Polyethylene oxide fatty acid amides;

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Primary and secondary alcohol ethoxylates;
Glyme, diglyme, triglyme and tetraglyme;
Mono-, di- and tripropylene glycol methyl
ethers and ether acetates;
5 Dimethyl adipate, succinate and glutarate;
Ethylene oxide/propylene oxide adducts with a
sucrose;
Ketones and polyketone polymers; and
mixtures thereof.

10

12. An improved polymer foaming composition of
Claim 11 wherein said halocarbon is selected from
the group consisting of:

15

CHClF_2 ; CH_2F_2 ; CHCl_2CF_3 ; CHClFCClF_2 ;
 CHClFCF_3 ; CHF_2CF_3 ; CHF_2CHF_2 ; CH_2FCF_3 and
mixtures thereof.

20

13. An improved polymer foaming composition of
Claim 12 further comprising a second blowing agent
gas selected from the group consisting of:

CFCl_3 ; CF_2Cl_2 ; $\text{CCl}_2\text{FCClF}_2$; $\text{CClF}_2\text{CClF}_2$;
 CCl_2FCH_3 ; CClF_2CH_3 ; $\text{CH}_2\text{FCH}_2\text{F}$; CH_3CF_3 ;
 CHF_2CH_3 ; CO_2 ; C_3 to C_6 hydrocarbons; methyl
formate; and mixtures thereof.

25

14. In a method of manufacturing an expanded
polymeric foam wherein a blowing agent expands as
the polymeric phase solidifies, the specific
improvement comprising the steps of:

30

(a) selecting a hydrogen-containing halocarbon as
the blowing agent; and
(b) adding an effective amount a hydrogen bond
forming blocking agent to reduce the permeation of
air into the foam or slow down the escape of
35 blowing agent from the foam.

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15. A method of Claim 14 wherein said hydrogen bond forming blocking agent is selected from the group consisting of: an organic ether, ester, ketone or mixtures thereof.

5

16. A method of Claim 14 or 15 wherein said hydrogen bond forming blocking agent is present in the range of from at least about 0.1 weight percent of said foam.

10

17. A method of Claim 14 or 15 wherein said hydrogen bond forming blocking agent is present in the range of from about 1.0 to about 20 weight percent of said foam.

15

18. A method of Claim 14 wherein said blocking agent is selected from the group consisting of:
- Polyethylene oxide polymers;
 - Ethylene oxide/propylene oxide copolymers;
 - 20 Polypropylene oxide polymers;
 - Polyethylene glycol mono- and dioleates;
 - Polyethylene glycol monostearates;
 - Alkylphenoxy polyethoxy ethanols;
 - Polyethylene oxide sorbitan monostearates and
 - 25 tristearates;
 - Polyethylene oxide fatty acid amides;
 - Primary and secondary alcohol ethoxylates;
 - Glyme, diglyme, triglyme and tetraglyme;
 - Mono-, di- and tripropylene glycol methyl
 - 30 ethers and ether acetates;
 - Dimethyl adipate, succinate and glutarate;
 - Ethylene oxide/propylene oxide adducts with a sucrose;
 - Ketones and polyketone polymers; and
 - 35 mixtures thereof.

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19. A method of Claim 14 wherein said halocarbon is selected from the group consisting of:
CHClF₂; CH₂F₂; CHCl₂CF₃; CHClFCClF₂;
CHClFCF₃; CHF₂CF₃; CHF₂CHF₂; CH₂FCF₃ and mixtures thereof.
20. A method of Claim 19 further comprising a second blowing agent gas selected from the group consisting of:
CFCl₃; CF₂Cl₂; CCl₂FCClF₂; CClF₂CClF₂;
CCl₂FCH₃; CClF₂CH₃; CH₂FCH₂F; CH₃CF₃;
CHF₂CH₃; CO₂; C₃ to C₆ hydrocarbons; methyl formate; and mixtures thereof.
21. An improved thermoplastic or thermoset polymer composition comprising:
(a) a polymer; and
(b) an effective amount of a hydrogen bond forming blocking agent to reduce the permeation of air into the foam or slow down the escape of blowing agent from the foam.
22. An improved polymer composition of Claim 21 wherein said hydrogen bond forming blocking agent is selected from the group consisting of: an organic ether, ester, ketone or mixtures thereof.
23. An improved polymer composition of Claim 21 wherein said hydrogen bonding blocking agent is selected from the group consisting of:
Polyethylene oxide polymers;
Ethylene oxide/propylene oxide copolymers;
Polypropylene oxide polymers;
Polyethylene glycol mono- and dioleates;
Polyethylene glycol monostearates;

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- Alkylphenoxy polyethoxy ethanols;
Polyethylene oxide sorbitan monostearates and
tristearates;
Polyethylene oxide fatty acid amides;
5 Primary and secondary alcohol ethoxylates;
Glyme, diglyme, triglyme and tetraglyme;
Mono-, di- and tripropylene glycol methyl
ethers and ether acetates;
Dimethyl adipate, succinate and glutarate;
10 Ethylene oxide/propylene oxide adducts with a
sucrose;
Ketones and polyketone polymers; and
mixtures thereof.
24. An improved intermediate for a polymer foam
15 composition comprising:
(a) a polyol, an isocyanate, or a resole; and
(b) an effective amount of a hydrogen bond
forming blocking agent to reduce the
permeation of air into the foam or slow down
20 the escape of blowing agent from the foam.
25. An improved intermediate for a polymer foam
composition of Claim 24 wherein said hydrogen bond
forming blocking agent is selected from the group
25 consisting of: an organic ether, ester, ketone or
mixtures thereof.
26. An improved intermediate for a polymer foam
composition of Claim 24 wherein said hydrogen
30 bonding blocking agent is selected from the group
consisting of:
Polyethylene oxide polymers;
Ethylene oxide/propylene oxide copolymers;
Polypropylene oxide polymers;
35 Polyethylene glycol mono- and dioleates;

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- Polyethylene glycol monostearates;
Alkylphenoxy polyethoxy ethanolis;
Polyethylene oxide sorbitan monostearates and
tristearates;
5 Polyethylene oxide fatty acid amides;
Primary and secondary alcohol ethoxylates;
Glyme, diglyme, triglyme and tetraglyme;
Mono-, di- and tripropylene glycol methyl
ethers and ether acetates;
10 Dimethyl adipate, succinate and glutarate;
Ethylene oxide/propylene oxide adducts with a
sucrose;
Ketones and polyketone polymers; and
mixtures thereof.
15
27. A B-side thermoset polymer foaming
composition comprising:
(a) a hydrogen-containing halocarbon; and
(b) an effective amount of a polyol to produce
20 a thermoset foam when reacted with an A-side,
and to simultaneously reduce the permeation
of air into the foam or slow down the escape
of blowing agent from the foam.
- 25 28. A B-side thermoset polymer foaming
composition of Claim 27 wherein said halocarbon is
selected from the group consisting of:
CHClF₂; CH₂F₂; CHCl₂CF₃;
CHClFCClF₂; CHClFCF₃; CHF₂CF₃; CHF₂CHF₂;
30 CH₂FCF₃ and mixtures thereof.
29. A B-side thermoset polymer foaming
composition of Claims 27 or 28 wherein said polyol
is selected from the group consisting of:
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polyethylene glycol, polypropylene glycol,
ethylene oxide/propylene oxide copolymer,
sucrose polyol; polyol containing ether,
ester or ketone groups, and mixtures thereof.

5

30. A B-side thermoset polymer foaming
composition of Claim 29 further comprising a
second blowing agent gas selected from the group
consisting of:

10

CFC1₃; CF₂Cl₂; CCl₂FCClF₂; CC1F₂CC1F₂;
CC1₂FCH₃; CC1F₂CH₃; CH₂FCH₂F; CH₃CF₃;
CHF₂CH₃; CO₂; C₃ to C₆ hydrocarbons; methyl
formate; and mixtures thereof.

15

31. A thermoset polymer foam composition produced
by reacting an isocyanate A-side in the presence
of a hydrogen-containing halocarbon; and an
effective amount of a polyol to produce a
thermoset foam and to simultaneously reduce the
permeation of air into the foam or slow down the
escape of blowing agent from the foam.

20

32. A thermoset polymer foam composition of Claim
31 wherein said halocarbon is selected from
the group consisting of:

25

CHClF₂; CH₂F₂; CHCl₂CF₃; CHClFCClF₂;
CHClFCF₃; CHF₂CF₃; CHF₂CHF₂; CH₂FCF₃ and
mixtures thereof.

30

33. A thermoset polymer foam composition of
Claims 31 or 32 wherein said polyol is selected
from the group consisting of:

polyethylene glycol, polypropylene glycol,
ethylene oxide/propylene oxide copolymer,

35

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sucrose polyol, polyol containing ether, ester or ketone groups, and mixtures thereof.

34. A thermoset polymer foam composition of Claim 33 further comprising a second blowing agent gas selected from the group consisting of:
- 5 CFC1₃; CF₂Cl₂; CCl₂FCClF₂; CClF₂CClF₂; CCl₂FCH₃; CClF₂CH₃; CH₂FCH₂F; CH₃CF₃; CHF₂CH₃; CO₂; C₃ to C₆ hydrocarbons; methyl formate; and mixtures thereof.
- 10
35. A method of manufacturing a closed cell foam comprising the steps of:
- 15 (a) admixing an effective amount of a hydrogen-containing halocarbon blowing agent to the B-side component of a polyurethane or polyisocyanurate foam such as to hydrogen bond said halocarbon with a polyol in said B-side component;
- 20 (b) contacting said admixture of step (a) with an effective amount of an A-side component of a polyurethane or polyisocyanurate foam for sufficient time and temperature to produce foaming; and
- 25 (c) recovering a fine closed-cell structured foam exhibiting improved k-factor relative to that predicted from VTC data.
36. A method of Claim 35 wherein said halocarbon is selected from the group consisting of:
- 30 CHClF₂; CH₂F₂; CHCl₂CF₃; CHClFCClF₂; CHClFCF₃; CHF₂CF₃; CHF₂CHF₂; CH₂FCF₃ and mixtures thereof.
- 35 37. A method of Claim 36 further comprising

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admixing a second blowing agent gas to said B-side wherein said second blowing agent gas is selected from the group consisting of:

5 CFC1₃; CF₂Cl₂; CCl₂FCClF₂; CClF₂CClF₂;
 CCl₂FCH₃; CClF₂CH₃; CH₂FCH₂F; CH₃CF₃;
 CHF₂CH₃; CO₂; N₂; C₃ to C₆ hydrocarbons;
 methyl formate; dimethyl ether; and mixtures
 thereof.

10 38. A method of Claim 35 further comprising
 admixing a second blowing agent gas to said B-side
 wherein said second blowing agent gas is selected
 from the group consisting of:

15 CFC1₃; CF₂Cl₂; CCl₂FCClF₂; CClF₂CClF₂;
 CCl₂FCH₃; CClF₂CH₃; CH₂FCH₂F; CH₃CF₃;
 CHF₂CH₃; CO₂; N₂; C₃ to C₆ hydrocarbons;
 methyl formate; dimethyl ether; and mixtures
 thereof.

20 39. A method of Claims 36 or 37 wherein said
 hydrogen-containing halocarbon blowing agent is
 HFC-134a.

25 40. A method of Claim 36 wherein said
 hydrogen-containing halocarbon blowing agent is
 HFC-134a and water is added to produce, in situ,
 CO₂ as a second blowing agent.

30 41. A method of Claims 36 or 37 wherein said
 hydrogen-containing halocarbon blowing agent is
 HFC-22.

35 42. A method of Claim 36 wherein said
 hydrogen-containing halocarbon blowing agent is
 HFC-22 and water is added to produce, in situ, CO₂

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as a second blowing agent.

43. A method of manufacturing a closed cell foam comprising the steps of:

5 (a) admixing an effective amount of HFC-134a blowing agent to the B-side component of a polyurethane or polyisocyanurate foam such as to hydrogen bond said HFC-134a with the polyol in said B-side component;

10 (b) contacting said admixture of step (a) with an effective amount of an A-side component of a polyurethane or polyisocyanurate foam for sufficient time and temperature to produce foaming; and

15 (c) recovering a fine closed-cell structured foam exhibiting improved k-factor relative to that predicted from VTC data.

44. A method of Claim 43 wherein said B-side component admixed with an effective amount of HFC-134a blowing agent further comprises an effective amount of water to produce, in situ, CO₂ as a second blowing agent.

- 25 45. A method of manufacturing a closed cell foam comprising the steps of:

30 (a) admixing an effective amount of HCFC-22 blowing agent to the B-side component of a polyurethane or polyisocyanurate foam such as to hydrogen bond said HCFC-22 with a polyether-containing polyol in said B-side component;

35 (b) contacting said admixture of step (a) with an effective amount of an A-side component of a polyurethane or

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polyisocyanurate foam for sufficient time and
temperature to produce foaming; and
(c) recovering a fine closed-cell structured
foam exhibiting improved k-factor relative to
that predicted from VTC data.

46. A method of Claim 45 wherein said B-side
component admixed with an effective amount of
HCFC-22 blowing agent further comprises an
effective amount of water to produce, in situ, CO₂
as a second blowing agent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/01130

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 J 9/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 08 J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT¹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR, A, 88849 (ICI) 31 March 1967 see claims A1a,b,A5,A8 ---	1-38,41, 41,42,45, 46
X	EP, A, 0001791 (ASAHI-DOW LTD) 16 May 1979 see claims 1-9; page 26, lines 1-14; page 27, lines 21-33 ---	1-23
X	EP, A, 0024324 (ASAHI-DOW LTD) 4 March 1981 see claims 1-6; page 9, lines 1-17; page 7, lines 19-31 ---	1-23
A	US, A, 3222304 (INGRAM) 7 December 1965 see claims 1-4 ---	1-23
./.		
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30th April 1991	11. 07. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	F.W. HECK 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	JP, A, 60110733 (ASAHI KASEI K.K.K.) 17 June 1985 see the whole abstract ---	1-23
X	EP, A, 0305084 (FIBERGLASS CANADA) 1 March 1989 see claims 1-10 -----	1-23

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9101130
SA 45043

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 88849		None	
EP-A- 0001791	16-05-79	JP-C- 1171115	17-10-83
		JP-A- 54111570	31-08-79
		JP-B- 57053810	15-11-82
		JP-C- 1139223	11-03-83
		JP-A- 54111571	31-08-79
		JP-B- 56046491	04-11-81
		JP-C- 1129829	24-12-82
		JP-A- 54111572	31-08-79
		JP-B- 57021526	08-05-82
		JP-C- 1192307	29-02-84
		JP-A- 54127473	03-10-79
		JP-B- 58025339	26-05-83
		JP-C- 1153518	30-06-83
		JP-A- 54148060	19-11-79
		JP-B- 56048535	16-11-81
		JP-C- 1129663	24-12-82
		JP-A- 54060363	15-05-79
		JP-B- 57022339	12-05-82
		JP-A- 54086564	10-07-79
		JP-B- 56046490	04-11-81
		JP-C- 1129473	24-12-82
		JP-A- 54087767	12-07-79
		JP-B- 56048534	16-11-81
		AU-B- 543377	18-04-85
		AU-A- 4090578	24-04-80
		CA-A- 1118950	23-02-82
		US-A- 4343913	10-08-82
		US-E- RE31744	20-11-84
EP-A- 0024324	04-03-81	JP-C- 1406366	27-10-87
		JP-A- 56024427	09-03-81
		JP-B- 62013981	30-03-87
		AU-B- 537578	05-07-84
		AU-A- 6095680	05-02-81
US-A- 3222304		None	

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US 9101130

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-60110733	17-06-85	None	
EP-A- 0305084	01-03-89	US-A- 4882364	21-11-89
		AU-A- 2143188	02-03-89
		JP-A- 1138244	31-05-89

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